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Editorial

Exploring the potential and challenges of molecular-squeeze adsorption in sponge-like crystals

Traditional desorption methods in porous sorbents rely heavily on energy-intensive processes such as heating, vacuum pumping, or inert gas purging [1]. While effective, these approaches incur substantial energy and operational costs, particularly for hydrocarbons with high boiling points or strong host–guest interactions [2]. This is the same case in the newly-developed macrocycle-based crystalline adsorbents, namely nonporous adaptive crystals (NACs). To address these challenges, a recent study published in *Angewandte Chemie International Edition* by Jie, Ma, and co-workers reported an innovative molecular-"squeeze" triggered desorption mechanism in NACs [3–5]. Specifically, ethyl acetate (EA) triggers guest desorption without penetrating the crystal pores or voids. Instead, EA molecules interact with the crystal surface through supramolecular forces, causing the adaptive closure of voids and the subsequent release of guest molecules. Unlike conventional sponges that rely on mechanical squeeze to deform themselves in the bulk for guest release, these macrocycle crystals undergo structural deformation at the molecular level and condensed phase when exposed to vaporized molecules. Because of the similar behavior between sponges and such NACs, the authors name them as sponge-like macrocycle crystals.

These sponge-like macrocycle crystals are composed of pillar[5]arene[1]quinone (EtP5Q1) molecules. The authors synthesized and characterized desolvated EtP5Q1 crystals, obtaining two polymorphic phases: EtP5Q1α (guest-loaded columnar conformer) and EtP5Q1β (guest-free collapsed conformer). Exposure to EA vapor induces a phase transition from EtP5Q1α to EtP5Q1β (Fig. 1a), driven by supramolecular interactions between EA molecules and the crystal surface. This process leads to the adaptive void closure and the release of guest hydrocarbons. Although neither EtP5Q1α nor EtP5Q1β exhibited selective uptake of benzene or cyclohexane, EtP5Q1α and EtP5Q1β acted as promising candidates for the selective separation of toluene and pyridine mixtures, offering valuable applications in chemical processes (Fig. 1b).

A key challenge in adsorptive separation is the ease of guest release, often requiring energy-intensive methods such as prolonged heating in a vacuum. Recently, Jie and co-workers have explored a novel desorption approach using vaporized EA to trigger the phase transition from CH@EtP5Q1 to EtP5Q1β. This transition triggers the release of adsorbed guests without the need for EA molecules to replace them. The process was confirmed by ^{1}H NMR spectra and PXRD patterns, which showed a gradual decrease in guest content and the transformation of the crystal structure.

Subsequent experiments with other guest-loaded EtP5Q1 crystals (*e.g.*, Py_3@EtP5Q1 and Bz_2@EtP5Q1) also demonstrated successful guest release *via* vaporized EA (Fig. 1c). The desorption mechanism was further explored using other molecules, revealing that those with longer chain lengths and ketone groups could also induce guest release. Notably, diethyl ether (DE), which lacks ketone groups, also demonstrated the same desorption effect, confirming that the release occurs through a "molecular-squeeze" mechanism at the crystal-vapor interface, rather than by dissolution and volatilization. This mechanism holds potential for improving the practical utility of these materials in industrial applications.

They elucidated the guest release mechanism by binding/lattice energy calculations and molecular dynamics (MD) simulations. MD simulations reveal a progressive increase in the host–guest intermolecular distance, leading to the collapse of the hexagonal columnar structure and guest release. The molecular-squeeze mechanism employs vaporized molecules as external forces to deform sponge-like macrocycle crystals. This interaction occurs at the crystal-vapor interface, where vaporized molecules like EA induce structural changes in the crystal without entering its pores. Instead, the deformation is driven by supramolecular interactions between the vapor molecules and the macrocycle surface, facilitating guest molecule release.

Compared with traditional desorption methods, this method operates entirely under ambient conditions (298 K, 1 atm), avoiding energy-intensive heating ($\geq$120 °C) or vacuum setups. It should be noted that EA-regenerated crystals still showed consistent performance across five cycles, maintaining guest recovery rates above 99% for toluene/pyridine separation.

By using vaporized EA to trigger guest release from the crystal, Jie and co-workers have provided a new method for desorption. This method, based on supramolecular interactions at the crystal-vapor interface, achieves energy-efficient separation. The molecular-squeeze method provides an energy-efficient and environmentally friendly alternative to conventional desorption techniques. By eliminating the need for heating or vacuum conditions, this method significantly reduces operational costs while ensuring material recyclability. While it works well for hydrocarbons, it could also be applied to other fields, such as medical separations, and gas separations, showing its versatility. Future research could focus on scaling this method for industrial use, ensuring adaptive crystals perform effectively on a larger scale. Combining this approach with other advanced materials could lead to even more innovative applications. This study not only advances separation technology but also opens new opportunities in materials science and related fields.

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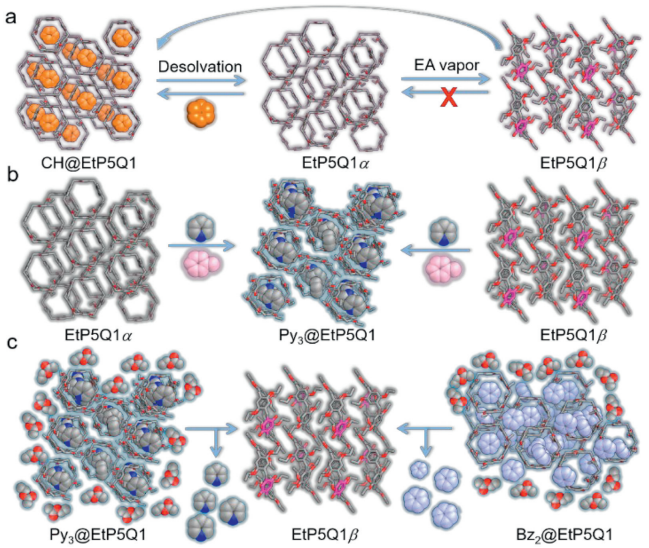

Fig. 1. (a) Schematic representation of phase transitions among EtP5Q1α, EtP5Q1β and CH@EtP5Q1. (b) Schematic representation of structural transformation from EtP5Q1α and EtP5Q1β to Py_3@EtP5Q1 upon capture of tolune/pyridine mixture. (c) Schematic representation of structural transformation from Py_3@EtP5Q1 and Bz_2@EtP5Q1 to EtP5Q1β upon exposure to vaporized EA. Reproduced with permission [3]. Copyright 2025, Wiley-VCH GmbH.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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